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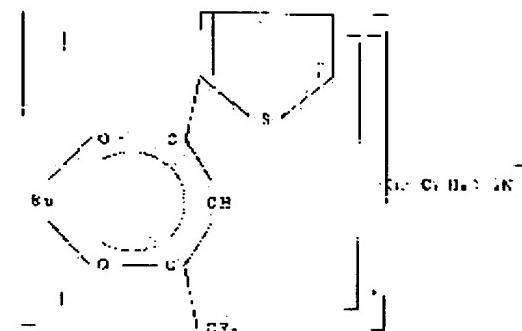
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(54) RECORDING FLUID

(57)Abstract:

PURPOSE: To obtain an ink jet recording fluid which emits red light when irradiated with ultraviolet rays and gives a record excellent in water resistance by incorporating a specific phosphor material into the fluid.

CONSTITUTION: This recording fluid contains, as a phosphor material, 0.005–3.0wt.% [tetra-4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato] europium complex which is represented by the formula, has a tetra-n-butylammonium salt as the counter ion, and emits red light of 600–650nm when irradiated with ultraviolet rays of 254–365nm. The fluid is prep'd. by dissolving the phosphor material and if necessary a binder component and other additives in a solvent such as N-methyl-2-pyrrolidone.



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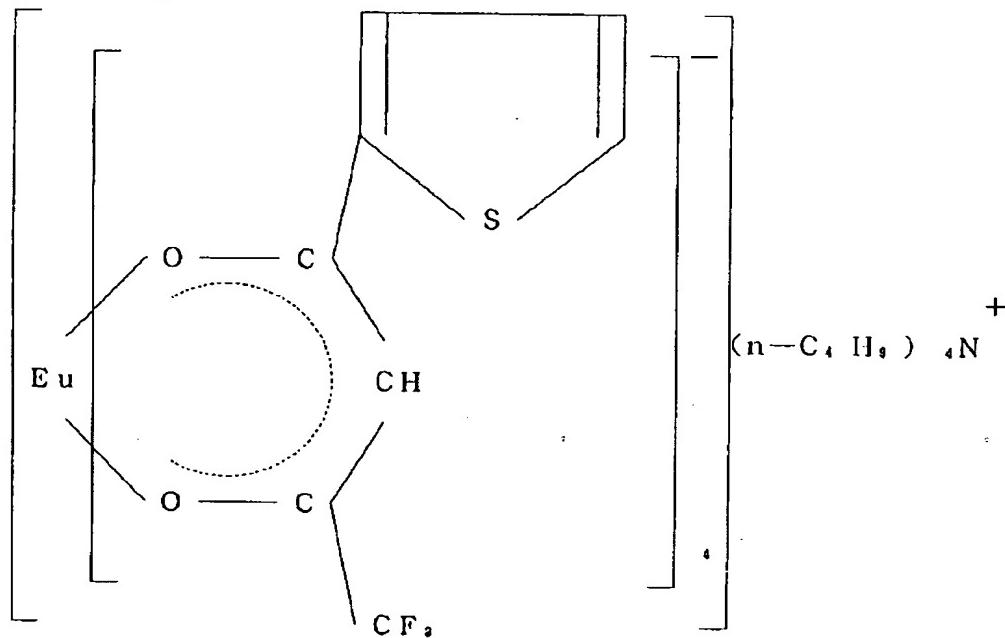
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CLAIMS**[Claim(s)]**

[Claim 1] Record liquid for ink jets characterized by including a fluorescence material shown by the following formula.

[Formula 1]

[Claim 2] Record liquid for ink jets according to claim 1 characterized by including a fluorescence material 0.005 to 3.0%.

[Claim 3] There is no claim 1 characterized by using a N-methyl-2-pyrrolidone as a solvent, and it is the record liquid for ink jets of a publication 2 either.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the record liquid which will be visualized if ultraviolet rays are irradiated. In more detail, when ultraviolet rays are irradiated, it is related with the record liquid excellent in the water resisting property which emits light in red for ink jets.

[0002]

[Description of the Prior Art] As record liquid for ink jets, what dissolved water soluble dye, such as acid dye, direct dye, and basic dye, in a glycol system solvent and water (JP,53-61412,A, JP,54-89811,A, JP,55-65269,A) is used well conventionally. As water soluble dye, in order to acquire the stability of record liquid, generally the soluble high thing to water is used. Therefore, the ink jet record object had the problem of producing a blot of the color of a record portion easily, when the water resisting property was bad and generally spilt water.

[0003] In order to improve such a waterproof defect, the structure of a color is changed or to prepare strong basic record liquid is tried (JP,56-57862,A). Moreover, aiming at waterproof improvement, using the reaction of the recording paper and record liquid well is also performed (JP,50-49004,A, JP,57-36692,A, JP,59-20696,A, JP,59-146889,A). Although these methods are obtaining the effect remarkable about the specific recording paper, when it uses for versatility except a chip and the specific recording paper in that constraint of the recording paper is received, with the record liquid which uses water soluble dye, sufficient water resisting property of a record object is not obtained in many cases..

[0004] Moreover, by irradiating ultraviolet radiation, although there were what distributed thru/or dissolved the oil color in retarder thinner, and a thing which dissolved the oil color in the volatile solvent as waterproof good record liquid, when it became the material which a record object is made to emit light and can be visualized, it was difficult [it] for there to be various constraint and to adjust such record liquid. Moreover, although it is hard to carry out a check from before with the usual light in various particular applications, it visualizes by special light or development of the ink which makes reading by the sensor possible is performed. What emits light purple like a fluorescent brightener was used for such [conventionally] a use. Since such a fluorescent brightener was a water color, it had the defect which is inferior to a water resisting property in a record object. Moreover, since the fluorescent brightener was widely used for paper, fiber, etc., it also had the defect of being hard to attach distinction with those luminescence. Moreover, although it dissolved when fluorescent dye was mixed with resin etc. and the organic solvent was used, and the fluorescent pigment which particle-sized fluorescent dye by resin could be used like a color, people are check **** things visually and the alphabetic character and graphic form which were displayed also when it had absorption also in the visible range and fluorescence was not applied to it were not able to be used for it as the so-called material of hiding ink.

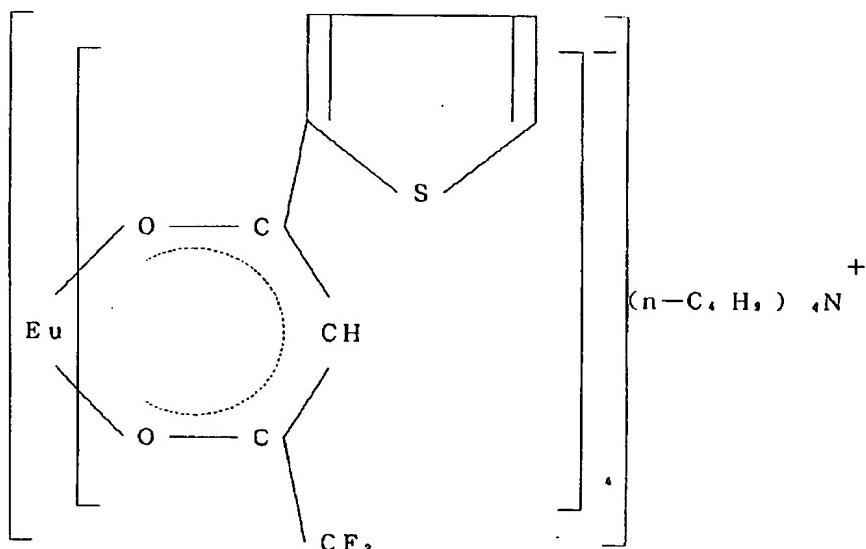
[0005]

[Problem(s) to be Solved by the Invention] The object of this invention is offering the record liquid for ink jets with which the waterproof good record object which emits light in red is obtained, when ultraviolet rays are irradiated.

[0006]

[Means for Solving the Problem] That is, this invention is record liquid for ink jets characterized by including a fluorescence material shown by the following formula.

[Formula 2]



[0007] This fluorescence material will emit light in red of 600-650nm, if 254-365nm ultraviolet rays are irradiated. Moreover, when not irradiating ultraviolet rays, since it is not coloring, discernment is not easy and is useful as the so-called material of hiding ink. This fluorescence material 4, 4, 4-trifluoro-1-(2-thienyl)-1, and 3-butanedione compound and perchloric acid europium with a sodium hydroxide Are manufactured by making it react in an acetone. Tetra--n-butyl ammonium salt Under the light, it is colorlessness, and under ultraviolet radiation, it is a tetrapod [which it has in a counter ion] 4 and 4, 4-trifluoro-1-(2-thienyl)-1, and 3-butane dionate] europium complex, and is [it has the property colored in red and / luminescence reinforcement is large and] excellent [reinforcement] in lightfastness etc. Although there is almost no solubility over water, since this fluorescence material has the solubility over a solvent enough, it is good, and extremely suitable as a fluorescence material for ink jets aiming at hidden printing. [of the water resisting property of a record object]

[0008] By this invention, it hides by using 0.005 to 3% of the weight into record liquid, since the luminescence reinforcement of this fluorescence material is strong, and detection

of the request as a printing object is possible. If fewer than this, reading of luminescence will become difficult, and when [than this range] more, it becomes easy to deposit, and it lifting-comes to be easy of troubles, such as blocking nozzle opening.

[0009] While ester solvents, such as ketones, such as an acetone which is excellent in the solubility of this fluorescence material, a methyl ethyl ketone, and a cyclohexanone, and ethyl acetate, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyl lactone, dioxane, toluene, a xylene, and high-boiling point petroleum solvents (for example, shell ZORU, the product made from shell chemistry, high ZORU, Nippon Oil make, etc.) be used as a solvent and an N-methyl - 2 - pyrrolidone is especially excellent in solvent power, since it is low volatility comparatively and is

[0010] The record liquid of this invention can be made to apply to a various printer and the various various recorded bodies by choosing the class of solvent, the existence of an activity of a binder, a class, an amount, etc., and adjusting viscosity, surface tension, electric conductivity, drying, etc. As a property of record liquid, although fitness changes with printers, generally the viscosity of 0.8-15cps, surface tension 20 - 60 dyn/cm are desirable. When using for the printer of a continuous method, it is desirable to adjust to the electric conductivity of 0.1 - 20mS degree. When aimed at the recorded body of the absorptivity of paper etc., it is desirable to use the following record liquid. That is, the fluorescence material of this invention, a solvent, and if needed, a binder component, an additive, etc. are dissolved and record liquid is produced.

[0011] A binder component is for fixing a fluorescence material good, and the solubility over the above-mentioned solvent is good, and can mention the following resin as what can adjust the viscosity of record liquid moderately. That is, the soluble resin which dissolves in the above-mentioned solvents, such as a vinyl chloride vinyl acetate copolymer, a polyvinylidene chloride, a cellulose type, a petroleum resin system, a phenol resin system, an epoxy system, an epoxy phenol system, natural resin systems (gum arabic, gelatin, etc.), acrylic, styrene-acrylic, a polyester system, a polyamide system, a polyurethane system, a butyral system, a silicon system, rosin, rosin modified resin (a phenol, a maleic acid, fumaric-acid resin, etc.), a rubber system, acrylamide, an alkyd These resin is needed when recording to the recorded body of non-permeability, and it is preferably used one to 5% of the weight 0.5 to 10% of the weight into record liquid. If fewer than this amount, a fluorescence material cannot fully be established to the recorded body of non-permeability. Moreover, when it increases more than this amount, the regurgitation stability of record liquid may be reduced. moreover, a possibility that generating of the fluorescence resulting from about [that a resin layer is thick and there is a possibility, alias a wrap, and of coming to be alike and causing lowering of luminescence of a fluorescence material], and resin will also become a failure about the perimeter of a fluorescence material -- **** -- it is.

In addition, an activity of resin obtains a still firmer water resisting property in a record object.

[0012] The following solvents can also be added and used as what prevents desiccation in the nozzle portion of record liquid, and solidification of record liquid, and prevents injection of stable record liquid, and desiccation by the passage of time of a nozzle as a solvent in this invention. As such a solvent, ethylene glycol, a diethylene glycol, propylene glycol, triethylene glycol, a polyethylene glycol, a glycerol, tetraethylene glycol, dipropylene glycol, the ketone alcohol, the diethylene-glycol monobutyl ether, ethylene-glycol-monobutyl-ether ethylene glycol monoethyl ether, 1, 2-hexandiol, a substitute pyrrolidone, 2 and 4, 6-hexane triol, tetra-furfuryl alcohol, 4-methoxy-4 methyl pentanone, etc. can be illustrated. Moreover, alcohols, such as a methanol, ethanol, and isopropyl alcohol, can also be used in the object which speeds up desiccation in the paper of record liquid. There is independent [no], it mixes and these solvents are used in 0 - 50% of range of record liquid.

[0013] At the time [like paper] whose printing hand-ed is, since it already carries out drying [of *****] for osmosis of the record liquid to paper early, a penetrating agent can be added. As such a penetrating agent, the glycol ether [, such as the diethylene-glycol monobutyl ether,], alkylene glycol, and polyethylene-glycol mono-lauryl ether, sodium lauryl sulfate, sodium dodecylbenzenesulfonate, sodium oleate, sodium dioctyl sulfosuccinate, etc. can be used. if [than this] more [these have effect sufficient by the amount of 5% or less used of record liquid and] -- a blot of printing and a paper omission (print through) -- a lifting -- it becomes less desirable

[0014] Moreover, since generating of the bubble at the time of circulation of record liquid or migration, and manufacture of record liquid is prevented, a defoaming agent can also be added. The following surfactants can also be added and used for the regurgitation stability of record liquid, and record image enhancement. As such a surfactant, anionic, nonionic, cation nature, and both the ionicity activator can be used. As an anionic activator **, a fatty-acid salt, an alkyl-sulfuric-acid ester salt, alkylaryl sulfonates, alkynaphthalenesulfonate, a dialkyl sulfonate, dialkyl sulfo succinate, alkyl diaryl ether disulfon acid chloride, alkyl phosphate, A polyoxyethylene-alkyl-ether sulfate, a polyoxyethylene-alkyl-aryl-ether sulfate, a naphthalene sulfonic-acid formalin condensate, polyoxyethylene alkyl phosphate, glycerol borate fatty acid ester, Polyoxyethylene glycerol fatty acid ester etc. can be illustrated.

[0015] As a nonionic activator, nonionic activators, such as polyoxyethylene alkyl ether, polyoxyethylene alkyl aryl ether, a polyoxyethylene oxypropylene block copolymer, a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, a glycerine fatty acid ester, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, a fluorine system, and a silicon system, can be illustrated. As

a cation nature activator, an alkylamine salt, quaternary ammonium salt, alkyl pyridinium salt, an alkyl imidazolium salt, etc. can be illustrated. As both ionicity activator, an alkyl betaine, an alkylamine oxide, phospha JIRUKORIN, etc. can be illustrated.

[0016] Although discernment by viewing cannot carry out the record object of this invention easily, it is possible to also make a record object easy to identify using a coloring agent. For this reason, a fluorescence material, and a pigment general together and a color general together can also be used into record liquid. However, in order to demonstrate a fluorescence property enough, it is necessary to stop this better ** to 2% or less of activity 3% or less of record liquid. As a color, fat dye, metallized dye, a disperse dye, etc. are used. These colors have the desirable purification color from which mineral salt was removed.

[0017] About manufacture of record liquid, a fluorescence material, a solvent, and if needed, resin, an additive, etc. are mixed, it stirs and dissolves, dilution and other additives are mixed if needed, and record liquid is manufactured. The disperser of a high speed besides stirring by the agitator which used the usual feather, an emulsifier, etc. can also perform mixed stirring. The mixed record liquid is enough filtered with the filter of 3micro or less of apertures in front of dilution or in the back. As for this better **, it is desirable to filter in FURUTA 1.0micro or less. In advance of filtration of a filter, filtration by centrifugal separation can also be used, this lessens blinding in filtration with a filter, and a filter estimated usable period becomes long.

[0018] Since the record liquid manufactured by this invention has the remarkably good water resisting property, it is suitably used as record liquid for ink jets, and it can be used in the field of the record object which is [bar code / the hiding alphabetic character of the document in office, a mark, marking of corrugated paper, numbering,] hard to recognize, and the record object which has a security function. Moreover, compared with the record liquid manufactured by colors, such as a fluorescent brightener, a water resisting property is also good, and the special image which is excellent in the shelf life of a record object can be formed.

[0019]

[Example] Hereafter, based on an example, this invention is further explained to details. The section and % express weight section and weight % among an example, respectively.

[0020] [Example 1] The following raw material was mixed and record liquid was produced. Fluorescence material The 0.3 sections The petroleum-solvent (shell ZORU AB made from shell chemistry) 30.7 section Dimethyl sulfoxide The 15.0 sections N-methyl-2-pyrrolidone After dissolving with a 54.0 section agitator for 20 minutes, it filtered with the 0.45micro membrane filter, and record liquid was manufactured. Viscosity was 4cps. This record liquid was put into the cartridge "thinkjet" by Hugh Red Packard, and it recorded on the regular paper. When 254nm ultraviolet rays were irradiated at the record object,

luminescence (near 620nm) of Orange or the cut red has been checked. Although water was hung down to the recording surface and the blot of ink was investigated, there are not a blot of ink and outflow and they had sufficient water resisting property.

[0021] [Example 2] The following raw material was mixed and record liquid was produced. A fluorescence material The 0.3 sections Methyl ethyl ketone The 80.0 sections Ethyl acetate The 5.0 sections N-methyl-2-pyrrolidone The 15.0 section Sodium thiocyanate After dissolving with a 1.0 section agitator for 20 minutes, it filters with a 0.45micro membrane filter, and it is record liquid. It manufactured. Viscosity was 1.3cps. This record liquid was put into the "Hitachi IJ printer" by Hitachi, Ltd., and it recorded on the regular paper. When 365nm ultraviolet rays were irradiated at the record object, luminescence of Orange or the cut red has been checked. Although water was hung down to the recording surface and the blot of ink was investigated, there are not a blot of ink and outflow and they had sufficient water resisting property.

[0022] [Example 3] The following raw material was mixed and record liquid was produced. Fluorescence material The 1.0 sections Vinyl chloride vinyl acetate copolymer (Union Carbide VYMH)

Section [1.0 /] Methyl Ethyl Ketone The 80.0 sections Ethyl acetate The 11.0 sections N-methyl-2-pyrrolidone The 2.0 sections Ethyl alcohol The 5.0 sections Sodium thiocyanate After dissolving with a 1.0 section agitator for 30 minutes, it filters with a 0.45micro membrane filter, and it is record liquid. It manufactured. Viscosity was 1.9cps. This record liquid was put into the "Hitachi IJ printer" by Hitachi, Ltd., and it recorded on the surface of the aluminum plate. When 254nm ultraviolet rays were irradiated at the record object, luminescence of Orange or the cut red has been checked.

[0023] [Example 4] The following raw material was mixed and record liquid was produced. A fluorescence material The 0.5 sections Vinyl chloride - vinyl acetate copolymer (Union Carbide VYMH) The 1.0 sections Methyl ethyl ketone The 80.0 sections Ethyl acetate The 11.0 sections N-methyl-2-pyrrolidone 1.0 section ethyl alcohol The 5.0 sections Sodium thiocyanate After dissolving with a 1.0 section agitator for 30 minutes, it filters with a 0.45micro membrane filter, and it is record liquid. It manufactured. Viscosity was 1.9cps. This record liquid was put into the "Hitachi IJ printer" by Hitachi, Ltd., and it recorded on the surface of the aluminum plate. When 254nm ultraviolet rays were irradiated at the record object, luminescence of Orange or the cut red has been checked. Moreover, when adhesion was tested using the mending tape (three em company make), there is also no exfoliation and the good printing condition was held.

[0024] [Example 5] The following raw material was mixed and record liquid was produced. A fluorescence material The 0.7 sections AT-100 (acrylic resin solution [by TOYO INK MFG. CO., LTD.] NV50%) The five sections Cyclohexanone The five sections Aluminum

chelating agent (Kawaken Fine Chemicals ARUGOMAS) 0.5 section methyl ethyl ketone 78 section toluene The six sections Sodium thiocyanate The 1.3 sections The ethyl-acetate 11.0 section N-methyl-2-pyrrolidone 1.0 section manufacture is a methyl ethyl ketone to a fluorescence material, a resin solution, and a chelating agent. the ten sections -- in addition, it dissolved well, and diluted with the remaining solvent after dissolution, the sodium thiocyanate was added, and record liquid was adjusted. Then, it filtered with the 0.8micro membrane filter, it put into the "Hitachi IJ printer" by Hitachi, Ltd., and recorded on the surface of the steel plate. When 254nm ultraviolet rays were irradiated at the record object, luminescence of Orange or the cut red has been checked. Although water was hung down to the recording surface and the blot of ink was investigated, there are not a blot of ink and outflow and they had sufficient water resisting property.

[0025] [Example 6] The following raw material was mixed and record liquid was produced. Fluorescence material The 0.5 sections Diethylene-glycol monobutyl ether The 5.0 sections Dimethyl sulfoxide The 15.0 sections N-methyl-2-pyrrolidone After dissolving with a 77.0 section agitator for 20 minutes, it filtered with the 0.45micro membrane filter, and record liquid was manufactured. This record liquid was put into the cartridge "thinkjet" by Hugh Red Packard, and it recorded on the regular paper. When 254nm ultraviolet rays were irradiated at the record object, luminescence (near 620nm) of Orange or the cut red has been checked. Although water was hung down to the recording surface and the blot of ink was investigated, there are not a blot of ink and outflow and they had sufficient water resisting property.

[0026] [Example 7] The following raw material was mixed and record liquid was produced. A fluorescence material The 0.4 sections Diethylene-glycol monobutyl ether The 5.0 sections Dimethyl sulfoxide The 5.0 sections Ethylene glycol The 2.0 sections Isopropyl alcohol The 10.0 sections N-methyl-2-pyrrolidone After dissolving with a 77.0 section agitator for 20 minutes, it filters with a 0.45micro membrane filter, and it is record liquid. It manufactured. This record liquid was put into the "mache LCP" by the mache company, and it recorded on corrugated paper. When 254nm ultraviolet rays were irradiated at the record object, luminescence (near 620nm) of Orange or the cut red has been checked. Although water was hung down to the recording surface and the blot of ink was investigated, there are not a blot of ink and outflow and they had sufficient water resisting property.

[0027]

[Effect of the Invention] By this invention, the good record liquid of the regurgitation stability excellent in solubility was able to be obtained. Moreover, a waterproof good record object can be obtained. since this record object can perform record which is hard to discriminate from the substrate of paper etc. and red luminescence is produced by

**ultraviolet radiation -- as a special record object -- reading by the sensor, and a secret letter
-- it can use for printing about a character and security etc.**